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# IMPROVEMENTS IN AN ELECTROSTATIC TRAP


## Field of the Invention

This invention relates to improvements in an
5    electrostatic trap (EST), that is, a mass analyser of the
type where ions injected into it undergo multiple
reflections within a field that is substantially
electrostatic during ion detection, i.e., any time dependent
fields are relatively small.  It relates in particular but
10    not exclusively to improvements in the Orbitrap mass
analyser first described in US-A-5,886,346.


## Background of the Invention

Electrostatic traps (ESTs) are a class of ion optical
15    devices where moving ions experience multiple reflections in
substantially electrostatic fields. Unlike in RF fields,
trapping in electrostatic traps is possible only for moving
ions. To ensure this movement takes place and also to
maintain conservation of energy, a high vacuum is required
20    so that the loss of ion energy over a data acquisition time
Tm is negligible.
There are three main classes of EST: linear, where ions
change their direction of motion along one of the
coordinates of the trap; circular, where ions experience
25    multiple deflections without turning points; and orbital,
where both types of motion are present. The so-called
Orbitrap mass analyser is a specific type of EST that falls
into the latter category of ESTs identified above. The
Orbitrap is described in detail in US-A-5,886,346.  Briefly,
30    ions from an ion source are injected into a measurement
cavity defined between inner and outer shaped electrodes.
The outer electrode is split into two parts by a
circumferential gap which allows ion injection into the

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measurement cavity.  As bunches of trapped ions pass a
detector (which, in the preferred embodiment is formed by
one of the two outer electrode parts), they induce an image
current in that detector which is amplified.

5          The inner and outer shaped electrodes, when energized,
produce a hyper-logarithmic field in the cavity to allow
trapping of injected ions using an electrostatic field.  The
potential distribution U(r,z) of the hyper-logarithmic field
is of the form

10

(1)          $$U(r,z) = \frac{k}{2}\left[z^2 - \frac{r^2}{2}\right] + \frac{k}{2}(R_m)^2 \cdot \ln\left[\frac{r}{R_m}\right] + C$$

where r and z are cylindrical coordinates and z=0 is the
plane of symmetry of the field ) C is a constant, k is the
field curvature and $R_m$ >0 is the characteristic radius.

15          In this field, the motion of ions with mass m and
charge q along the axis z is described as a simple harmonic
oscillator with an exact solution for q,k>0:

(2)          $$z(t) = A_z \cdot \cos(\omega_0 t + \theta)$$

20

where

(3)          $$\omega_0 = \sqrt{\frac{qk}{m}}$$

and $\omega_0$ thus defines the frequency of axial oscillations in
25   radians per second, and $A_z$ and $\theta$ are the amplitude and phase
of axial oscillations, respectively.

          Whilst the foregoing discusses the theoretical
situation, in which the electrodes are of ideal hyper-
logarithmic shape, in reality there is a limit to the
30   accuracy with which any practical construction can

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approximate that ideal geometry.  As discussed in
"Interfacing the Orbitrap Mass Analyser to an Electrospray
Ion Source", by Hardman et al, Analytical Chemistry Vo. 75,
No. 7, April 2003, any divergence from the ideal electrode
5    geometry, and/or inclusion of electrical perturbations, will
result in a perturbation to the ideal field which in turn
will transform the harmonic axial oscillations of the ideal
field into non-linear oscillations.  This in turn may result
in a reduction in mass accuracy, peak shape and height, and
10   so forth.
        The present invention, in general terms, seeks to
address problems arising from the non-ideal nature of a real
electrostatic trap.


15                        Summary of the Invention
        Against this background, aspects of the present
invention provide for an electrostatic ion trap in which
deliberate non-linearities or perturbations are introduced
to the field so as to control or constrain the rate of phase
20   separation of ions within a given bunch (of single m/z).  In
particular, the present invention provides, in a first
aspect, an electrostatic ion trap for a mass spectrometer,
comprising an electrode arrangement defining an ion trapping
volume, the electrode arrangement being arranged to generate
25   a trapping field defined by a potential
$U'(r,\varphi,z)=U(r,\varphi,z)+W$, where $U(r,\varphi,z)$ is an ideal potential
which traps ions in the Z-direction of the trapping volume
so that they undergo substantially isochronous oscillations
and where W is a perturbation to that ideal potential
30   $U(r,\varphi,z)$, wherein the geometry of the electrode arrangement
generally follows one or more lines of equipotential of the
ideal potential $U(r,\varphi,z)$ but wherein at least a part of the
electrode arrangement deviates to a degree from that ideal

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potential $U(r, \varphi, z)$ so as to introduce the perturbation $W$
into the said trapping field, the degree of deviation from
the ideal potential $U(r, \varphi, z)$ being sufficient to result in
the relative phases of the ions in the trap shifting over
5    time such that at least some of the trapped ions have an
absolute phase spread of more than zero but less than about
$2\pi$ radians over an ion detection period $T_m$.

According to a second aspect of the present invention,
there is provided an electrostatic ion trap for a mass
10   spectrometer comprising an electrode arrangement defining an
ion trapping volume, the electrode arrangement being
arranged to generate a trapping field defined by a potential
$U(r, \varphi, z)$ where $U(r, \varphi, z)$ is a potential which traps ions in
the Z-direction of the trapping volume so that they undergo
15   substantially isochronous oscillations, wherein the trap
further comprises field perturbation means to introduce a
perturbation $W$ to the potential $U(r, \varphi, z)$ so as to enforce a
relative shift in the phases of the ions over time such that
at least some of the trapped ions have an absolute phase
20   spread of more than zero but less than about $2\pi$ radians over
an ion detection period $T_m$.

The specific description provides a detailed
theoretical analysis of the non-ideal electrostatic trap and
the manner in which perturbations $W$ affect the overall
25   performance of the mass analyser. In general terms,
however, it may be noted that there are a very large number
of trap parameters which affect the mass analysis to varying
degrees, including the degree to which the field generation
means approximates the ideal electric field, the accuracy of
30   various dimensions of the trap both in absolute terms and
relative to other components of the trap, the accuracy and
stability of any voltages applied to generate the field, and
so forth. Nevertheless, in broad terms these may be

classified into geometric distortions, such as "stretching" of the shape, shifting of the spatial location of the electrodes relative to an equipotential of the ideal field $U(r,\varphi,z)$, oversizing or undersizing the electrodes in one or

5   more dimensions etc, and applied distortions such as voltages applied to the trapping and/or to additional distortion electrodes (eg end cap electrodes), or applied magnetic fields, etc. Of course, whilst it is possible to create the appropriate perturbation W using only one of

10  these (geometric or applied distortion), a suitable perturbation could of course be created using a combination of both a geometric and an applied distortion.

In terms of the effect upon the trapped ions, the non-ideal nature of the trap results in one of two general

15  situations. In the ideal trap, the oscillations in the axial (Z) direction have a frequency $\omega_0$ that is independent of amplitude (apart from a small, asymptotic shift due to space charge effects, regarding which, see later). For a non-ideal trap, and assuming that W, the perturbation, is a

20  function of z (at least), the oscillations in the z direction of ions are no longer independent of amplitude. Instead, the ions either spread out (separate) in phase over time or compress (bunch) together in phase. In the case of phase bunching, this results in various undesirable

25  artefacts such as the so-called "isotope effect" (explained below), poor mass accuracy, split peaks, poor quantitation (i.e. a distortion of the relation between measured and real intensities of peaks) any one of which may be fatal to the analytical performance of the trap. In the case of phase

30  separation, the spread of phases will continue to increase with time. Once the phase spread exceeds $\pi$ radians, ions start to move with opposite phases, resulting in

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compensating image currents that progressively reduce the
overall signal.

If the phase spreading occurs rapidly (relative to a
measurement time $T_m$), then the desirable part of the signal
5     is essentially lost whilst the signal resulting from the
phase bunched ions is analytically poor or useless.  The
present invention in a first aspect provides for a trap with
parameters optimized so as to constrain the rate of increase
in phase spread.  It is likely that a real trap will have
10    parameters that result in a perturbation to the ideal field
W which cause some phase  spreading.  However, if the phase
spreading is constrained so as to keep it below about $2\pi$
radians, for a time period commensurate with a trap
measurement period $T_m$, then non-bunched ions will be
15    detected without degradation in analytical performance.

An alternative way of looking at this is to consider
the rate of decay of the 'transient' detected by the
detection means.  Typically, such a transient is generated
by measuring the image current induced in the detection
20    means by ions in the trap.  A trap in which there is a rapid
decay in the amplitude of the transient, in the time domain,
exhibits a poor analytical performance, and in particular
the mass accuracy tends to be poor in the Fourier
transformed signal.

25    Thus in accordance with a third aspect of the present
invention, there is provided an ion trap for a mass
spectrometer, comprising:  electric field generation means
to produce an electric field within which the ions may be
trapped;  and detection means to detect ions according to
30    their mass to charge ratio;  wherein the electric field
generation means is arranged to produce an electric trapping
field which traps ions so that they describe oscillatory
motion in which the period of oscillations is dependent upon

the amplitude of oscillations thereof, so as to cause a
shift in the relative phase of ions in the trap over time,
wherein the detection means is arranged to generate a time
domain transient from the ions in the trap, the transient
5       containing information on those ions, and further wherein
the parameters of the trapping field are arranged such that
the detected transient decays from a maximum amplitude to no
less than a) 1%; b) 5%; c) 10%; d) 30%; e) 50% over an ion
detection time $T_m$.

10          In yet another aspect of the invention there is
provided an electrostatic ion trap for a mass spectrometer
comprising: electric field generation means to produce an
electric field within which the ions may be trapped;  and
detection means to detect ions according to their mass to
15      charge ratio, wherein the electric field generation means is
arranged to produce an electric field of the form, in
cylindrical coordinates:

$$U(r, \phi, z) \ = \ \frac{k}{2}\left[z^2 - \frac{r^2}{2}\right] + \frac{k}{2}(R_m)^2 \cdot \ln\left[\frac{r}{R_m}\right] + W(r, \phi, z)$$

20

where U is the field potential at a location $r, \phi, z$;  k is
the field curvature;  $R_m > 0$ is the characteristic radius, and
$W(r, \phi, z)$ is a field perturbation, and further wherein W is
a function of r and/or $\phi$ but not z, or wherein W is a
25      function of at least z but wherein, in that case, the field
perturbation W causes the  period of oscillation of at least
some of the ions along the z axis of the trap to increase
with the increase in the period of oscillation in that z
direction.

30          Various features of the trap have been ascertained
through experiment to result in a perturbation that causes

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phase bunching to dominate, with the peak from non-bunched
ion packets being lost because of a rapid growth in phase
shift.  Preferred features of the present invention propose
controlled distortions to the trap geometry, configuration

5    and/or applied voltages so as to constrain the rate of
growth of non-bunched ion packets so that the phase shift
does not exceed about $2\pi$ radians over the time scale of ion
measurement.

In accordance with a further aspect of the present

10   invention there is provided an electrostatic ion trap for a
mass spectrometer comprising: electric field generation
means to produce an electric field within which the ions may
be trapped;  and detection means to detect ions according to
their mass to charge ratio; wherein the electric field

15   generation means is arranged to produce an electric trapping
field which traps ions so that they describe oscillatory
motion in which the period of oscillations is dependent upon
the amplitude of oscillations thereof, so as to cause a
shift in the relative phase of ions in the trap over time,

20   and further wherein the parameters of the trapping field are
arranged such that the spread of phases of at least some of
the ions in the trap to be detected is greater than zero but
less than about $2\pi$ radians over an ion detection time $T_m$.

The invention also extends to a method of trapping ions

25   in an electrostatic trap having at least one trapping
electrode, comprising:  applying a substantially
electrostatic trapping potential to the or each trapping
electrode, so as to generate an electrostatic trapping field
within the trap, for trapping ions of a mass to charge ratio

30   m/q in a volume V such that they undergo multiple
reflections along at least a first axis z; and applying a
distortion to the geometry of the trap, and/or to the

trapping potential applied to the or each trapping
electrode, so as to cause a perturbation in the
electrostatic trapping field which results in at least some
of the ions of mass to charge ratio m/q to undergo a
5    separation in phase of no more than about $2\pi$ radians over a
measurement time period $T_m$. Preferably, such separation
should be positive.

The invention also extends to a method of trapping ions
in an electrostatic trap having at least one trapping
10   electrode, comprising:   applying a substantially
electrostatic trapping potential to the or each electrode,
so as to generate an electrostatic trapping field within the
trap, for trapping ions in a volume V such that they undergo
multiple reflections, along at least a first axis z, with a
15   period of oscillation $\tau$ increasing with increasing amplitude
of oscillation $A_z$ of ions trapped in the field over the
volume V.

In still a further aspect of the invention, there is
provided a method of determining the acceptability or
20   otherwise of an electrostatic trap, comprising supplying a
plurality of ions to the trap; detecting at least some of
the ions in the trap; generating a mass spectrum therefrom;
and either (a) ascertaining whether or not the peaks in that
mass spectrum are split, split peaks being indicative of a
25   poorly performing trap, and/or (b) determining the relative
abundances of isotopes of a known ion in the mass spectrum,
the degree to which these relative abundances correspond
with predicted (theoretical or naturally occurring)
abundances being indicative of the acceptability of the
30   trap.

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Brief Description of the Drawings

The invention may be put into practice in a number of ways and some specific embodiments will now be described by way of example only and with reference to the accompanying
5    Figures in which:

Figure 1 shows a schematic arrangement of a mass spectrometer including an electrostatic trap and an external storage device;

Figure 2 shows plots of the dependence of the amplitude
10    of oscillation on the period of oscillation in an ideal and a non-ideal electrostatic trap;

Figure 3 shows the change in relative phase of ions in the electrostatic trap as a function of time t, in the presence of various perturbing factors;

15    Figure 4 shows a side sectional view of an electrostatic trap in accordance with a first embodiment of the present invention;

Figure 5 shows a side sectional view of an electrostatic trap in accordance with a second embodiment of
20    the present invention;

Figure 6 shows a side sectional view of an electrostatic trap in accordance with a third embodiment of the present invention;

Figure 7 shows a side sectional view of an
25    electrostatic trap in accordance with a fourth embodiment of the present invention;

Figures 8a-8d show mass spectra from a first sample at around m/z = 195, with increasing degrees of non-linearity introduced into the electrostatic field such that
30    increasingly rapid phase separation occurs;

Figures 9a-9d show mass spectra from a second sample at around m/z = 524, with increasing degrees of non-linearity

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introduced into the electrostatic field such that
increasingly rapid phase separation occurs;

Figure 10a shows a transient produced from an EST with
optimised parameters, resulting in a gradual spread of
5    phases and a gradual decay in the transient; and

Figure 10b shows a transient produced from an EST with
poor parameters, resulting in a rapid spread of phases and a
rapid initial decrease in the magnitude of the transient.


10        Detailed Description of the Preferred Embodiment
Referring first to Figure 1, a schematic arrangement of
a mass spectrometer including an electrostatic trap and an
external storage device is shown.  The arrangement of
Figure 1 is described in detail in commonly assigned
15   WO-A-02/078046 and will not be described in detail here. A
brief description of Figure 1 is, however, included in order
better to understand the use and purpose of the
electrostatic trap to which the present invention relates.

As seen in Figure 1, the mass spectrometer 10 includes
20   a continuous or pulsed ion source 20 which generates gas-
phase ions.  These pass through an ion source block 30 into
an RF transmission device 40 which cools ions.  The cooled
ions then enter a linear ion trap acting as a mass filter 50
which extracts only those ions within a window of mass
25   charge ratios of interest.  Ions within the mass range of
interest then proceed via a transfer octapole device 55 into
a curved trap 60 which stores ions in a trapping volume
through application of an RF potential to a set of rods
(typically, quadrupole, hexapole or octapole).

30        As explained in more detail in the above-mentioned
WO-A-02/078046, ions are held in the curved trap 60 in a
potential well, the bottom of which may be located adjacent
to an exit electrode thereof.  Ions are ejected orthogonally

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out of the curved trap 60 into a deflection lens arrangement
70 by applying a DC pulse to the exit electrode of the
curved trap 60.  Ions pass through the deflection lens
arrangement 70 and into an electrostatic trap 80.  In Figure
5   1, the electrostatic trap 80 is the so-called "Orbitrap"
type, which contains a split outer electrode85, and an inner
electrode 90.  Downstream of the Orbitrap 80 is an optional
secondary electron multiplier (not shown in Fig 1), on the
optical axis of the ion beam.

10        In use, a voltage pulse is applied to the exit
electrode of the curved trap 60 so as to release trapped
ions in an orthogonal direction.  The magnitude of the pulse
is preferably adjusted to meet various criteria as set out
in WO-A-02/078046 so that ions exiting the curved trap 60
15   and passing through the deflection lens arrangement 70 focus
in time of flight. The purpose of this is to cause ions to
arrive at the entrance to the Orbitrap as a convolution of
short, energetic packets of similar mass to charge ratio.
Such packets are ideally suited to an electrostatic trap
20   which, as will be explained below, requires coherency of ion
packets for detection to take place.
          The ions entering the Orbitrap 80 as coherent bunches
are squeezed towards the central electrode 90.  The ions are
then trapped in an electrostatic field such that they move
25   in three dimensions within the trap and are captured
therein.  As is explained in more detail in our commonly
assigned US Patent No. US-A-5,886,346, the outer electrodes
of the Orbitrap 80 act to detect an image current of the
ions as they pass in coherent bunches.  The output of the
30   ion detection system (the image current) is a "transient" in
the time domain which is converted to the frequency domain
and from there to a mass spectrum using a fast Fourier
transform (FFT).

Having described the mode of operation of the Orbitrap
80 and its typical use within a mass spectrometer
arrangement 10, a theoretical analysis of the trapping of
ions within the Orbitrap 80 will now be provided, in order
5    to gain a better understanding of the present invention.


Motion in an Ideal Field
As explained in US-A-5,886,346, the ideal form of
electrostatic field within the Orbitrap 80 has a potential
10   distribution U(r,z), as defined in Equation (1) of the
introduction above. Note that, in Equation (1), the
parameter C is a constant. In this field, the motion of
ions with mass m and charge q along the axis z is described
as a simple harmonic oscillator with an exact solution
15   defined in Equation (2) above, with $\omega_0 = \sqrt{(qk/m)}$, see
Equation 3 above. In other words, the period of oscillation
$\tau (= 2\pi / \omega_0)$ in that z direction is independent of the
amplitude of oscillation of ions in the z direction, $A_z$.


20

Motion in a Perturbed Field: 2D Perturbation
In constructing a real electrostatic trap, the field
defined by Equation (1) can only be approximated due to
finite tolerances.
25   In cylindrical coordinates $(r, \phi, z)$, the potential
distribution U can be written, generally, as:


(4)   $U(r, \phi, z), = \frac{k}{2}\left(z^2 - \frac{r^2}{2}\right) + \frac{k}{2}(R_m)^2 \cdot \ln\left[\frac{r}{R_m}\right] + W(r, \phi, z)$ .


30   Here, the parameters of the equation are as defined in
connection with Equation (1), save that the constant C is

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replaced by a field perturbation W which is, in its most
general form, three-dimensional.

   If we consider the situation where W does not depend on
z, and also satisfies the Laplace equation given by Equation
5  (5) below:

(5)                          $\Delta W(r,\varphi) = 0$

   It may be shown that the motion of ions in the
z direction remains defined by Equations (2) and (3) above.
10  In particular, the period of oscillation τ ($=2\pi/\omega_0$) remains
independent on the amplitude of oscillation $A_z$ in the
z direction.  The general solution to Equation (5), in (xy)
coordinates, may be written as

15  (6)  $U(x,y) = -\frac{k}{4}[x^2 - y^2]a + \left[A.r^m + \frac{B}{r^m}\right]\cos\left\{m.\cos^{-1}\left(\frac{x}{r}\right) + \alpha\right\} + b\cdot\ln\left(\frac{r}{D}\right) +$

   $E\cdot\exp(F\cdot x)\cos(F\cdot y + \beta) + G\exp(H\cdot y)\cos(H\cdot x + \gamma)$

where $r=\sqrt{(x^2 + y^2)}$, $\alpha,\beta,\gamma,a,A,B,D,E,F,G,H$ are arbitrary constants
(D>0), and j is an integer.  It should be noted that
20  Equation (6) is general enough to remove completely any or
all of the terms in Equation (1) that depend upon r, and
replace them with other terms, including expressions in
other coordinate systems (such as elliptic, hyperbolic, etc.
systems of coordinates).  However, such great deviations
25  from axial symmetry are rarely advantageous in practice.
The construction of an electrostatic trap is, in other
words, preferably such that the perturbation W remains
small.  For example, matching elliptical deformation of both
the inner and the outer electrodes of the Orbitrap, or
30  parallel shifting of the inner electrode relative to the

outer electrode along the x- or y-coordinate, will have no
influence on Equations (2) and (3) (such that the period of
oscillation τ remain independent of the amplitude of axial
oscillations), whilst the tolerance requirements on such
5    deformations for the construction of a trap which operates
within acceptable boundaries are less strict.


Motion in a Perturbed Field:    Problems with 3D Perturbations
        The primary difficulties with a real electrostatic trap
10   arise in the case where the perturbation W does depend on z
(either with or without an additional dependence upon r
and/or $\phi$).  In this case, Equations (2) and (3) are no
longer exactly true and the period of oscillation τ becomes
a function of the amplitude of oscillation $A_z$.  The vast
15   majority of manufacturing imperfections, to be discussed in
further detail below, result in a perturbation W that has a
dependence upon z at least (and, normally, also cross-terms
$r^l z^m \cos^n(\phi)$, where $l$, $j$, $n$ are integers).  The effect itself
is very complex.  However, it is possible to obtain a useful
20   and meaningful generalisation by considering two simple but
contrasting situations.
        Referring to Figure 2, some plots of the dependence of
the period of oscillation τ upon the amplitude of
oscillation of ions in the z direction are shown. The dotted
25   line 200 represents the ideal situation where there is no
perturbation (that is, the situation of Equation (1) or,
alternatively, where the perturbation is not dependent upon
z (as described in "Motion in a Perturbed Field:    2D
Perturbation" above).  The period of oscillation of ions in
30   the electrostatic trap remains constant, for a given mass to
charge ratio, regardless of the amplitude of those
oscillations.

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Where the electrostatic field is slightly non-linear
(Equation (4)) and the perturbation W is dependent upon z,
the period of oscillation $\tau$ starts to depend upon $A_z$.  Line
220 in Figure 2 illustrates, simplistically, the case where

5    higher amplitudes result in shorter periods of oscillation
T.  Ions in the beam are spread over a range of amplitudes
$\Delta z$ and have a spread of initial phases $\Delta \theta_z$.  It will of
course be understood that the real dependence of the period
of oscillation $\tau$ upon amplitude of oscillation $A_z$ is most

10   unlikely to be linear for all possible $A_z$, as line 220
suggests, but showing a linear, monotonically decreasing
period of oscillation $\tau$ with increasing $A_z$ permits more
straightforward explanation.  The situation where the
dependence of period upon amplitude does not increase or

15   decrease in a linear, monotonous fashion will be explored
below.

For ions in the ideal field of Equation (1), and in
absence of any collisions, the oscillation according to
Equations (2) and (3) without shift of parameters will

20   result in a fixed phase spread $\Delta \theta$ over time t.  This is
shown as dotted line 300 in Figure 3.

Where the perturbation results in a slightly non-linear
electric field, due to the perturbed potential distribution
defined by equation (4), and that perturbation has a

25   dependence upon z, the ions will still move in accordance
with Equations (2) and (3).  However, ions will now have a
phase $\theta$ which changes with time t.  In the case of a
dependence of period $\tau$ on amplitude $A_z$ that is as shown by
line 220 in Figure 2 ($\tau$ decreases with increasing $A_z$), the

30   spread of phases will increase with time.  This is because
ions with a higher $A_z$ will move faster, relatively speaking,
and ions with lower $A_z$ will move relatively slower.  The

increase in the spread of phases as a consequence is shown
by dotted line 310 in Figure 3.

At the point where the phase spread exceeds $\pi$ radians,
ions start to move with opposite phases.  This in turn

5    compensates image currents of each other which progressively
reduces the overall signal.

There is a minimum detection period within the
Orbitrap.  The longer the detection period, the higher the
resolution.  On the other hand, extended measurement periods

10   result in a phase spread shift that exceeds $\pi$ radians.
Therefore, it may be seen that a first restriction upon the
manufacture of a real electrostatic trap is that any
perturbation introduced should result in a net change in
relative phase of no more than about $2\pi$ radians, preferably

15   no more than $\pi$ radians, over a sufficiently long
measurement period $T_m$.

In fact, in a real trap, the increase in phase spread
over time is generally not simply a result of a slightly
non-linear field (due to a perturbation of the potential,

20   W).  When the number of ions in a beam is increased beyond a
certain level (typically, beyond 10,000 to 100,000 ions),
ion-ion interactions start to affect ion motion, as a
consequence of space charge.  In the ideal field (1), this
results in a spreading of an ion beam that slows down with

25   time, as the ion packets becomes large enough that the
distance between ions reaches a high level.  This small,
time-dependent drift of phase $\theta$, which is a consequence of
space charge and  occurs even in the absence of a
perturbation of the potential, is a known phenomenon and is

30   shown schematically as line 320 in Figure 3.  It will be
seen the line 320 asymptotically approaches a line with a
non-zero slope.

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In the case of a non-linear electric field, due to the
perturbed potential distribution described by equation (4),
which results in a period of oscillations $\tau$ that increases
with increasing amplitude $A_z$ (line 210 of Figure 2), this
5    small time-dependent phase drift resulting from space charge
effects is still present.  In this case, however, the space
charge effects represented by line 320 are associative with
the increase in phase resulting from the dependence of
period on amplitude given by line 210 in Figure 2 and shown
10   as line 310 in Figure 3.  Adding lines 310 and 320 results
in line 330 of Figure 3.  Thus it will be seen that, even
with the effects of space charge, the consequence of a
perturbation on the ideal field which results in a period of
oscillations decreasing with increasing amplitude $A_z$ is that
15   the line 330 reaches the $\pi$ radian phase shift in less time.
As explained above, this means that, for a given
construction of electrostatic trap, the space charge effect
merely reduces the maximum suitable measurement period $T_m$.

The consequences of a perturbation W resulting in a
20   period of oscillation $\tau$ that decreases with amplitude $A_z$ is
more problematic, however.  Line 220 in Figure 2
illustrates, again schematically and for the purposes of
example only, this situation.  Physically, the consequence
of a dependence such as is shown in line 220 of Figure 2 is
25   that ions are "bunched" together.  The reason for this is as
follows.  The small time-dependent drift of phase $\theta$
resulting from space charge is still present.  However, this
combines with the effect of the non-linear field which
results in the dependence of T on $A_z$ shown in line 220 of
30   Figure 2 to produce a shift in phase illustrated by line 340
of Figure 3.

One possible mechanism for this counter-intuitive behaviour is as follows. Ions at the edge of the ion beam are pushed to smaller or larger $A_z$. For example, an ion on the right-hand edge of the range of amplitudes $A_z$ of Figure 2 is pushed by the space charge effect of other ions to a larger $A_z$, at the same time lagging in phase $\theta$. As a result of the dependence shown by line 220, however, a larger amplitude $A_z$ corresponds to a lower period of oscillation $\tau$ (and a higher frequency $\omega_0$) of oscillations, so that the ion is forced to catch up in phase $\theta$ and return to the same phase as ions in the middle of the beam.

Similarly, ions that are pushed to a smaller amplitude $A_z$ and forward in phase $\theta$ become slower and also return back to the same phase as ions in the middle of the beam. As a result, rather than continuously increasing the ion beam phase spread (as occurs in the other situation resulting in line 330 above), the ion beam stops increasing its phase spread. For certain non-linearities, as shown by line 340, the phase spread may even begin to decrease over time.

Whilst at first glance this may appear desirable, in fact it has a number of consequences which are at best highly undesirable, and at worst can result in an unacceptably poor performance of the electrostatic trap. For example, the peak frequency will shift as a consequence of the curve 340, which in turn affects the measured m/q. In some cases, for example when non-linearity varies significantly over the cross-section of the ion beam, the beam may even split into two or more sub-beams, each with its own behaviour. This will result, in turn, in split peaks (shown in Figures 8d and 9d in particular, regarding which, see below), poor mass accuracy, incorrect isotopic ratios (as an intense ion beam decays more slowly than a less intense beam), poor

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quantitation etc. Moreover, these effects may well be different for differing mass to charge ratios, so that, even if a device can be optimised to minimise phase bunching for a specific mass to charge ratio, this may not improve (or
5    may even make worse) the situation with other mass to charge ratios.

In reality, the perturbation W will have a complex structure such that different parts of the same ion beam, with the same mass to charge ratio, may experience vastly
10   different effects. For example, one part of the beam could be self-bunched with one average rate $(d\theta/dt)_1$, a second part of the beam may experience rapid phase spreading (within time $t \ll T_m$), with a third part of the beam self-bunched at a different rate $(d\theta/dt)_2$. This will result in a split peak
15   with a part of the peak at a frequency $\omega_0 + (d\theta/dt)_1$ and another part at a different frequency $\omega_0 + (d\theta/dt)_2$. The second part of the beam, which has experienced rapid phase expansion, will be greatly suppressed, again as explained above. Even more complicated scenarios can be envisaged
20   and, rapidly, the mass accuracy of the device can be fatally compromised.

The foregoing discussion leads to the following conclusions. There is nothing that can be done from an electrostatic field point of view to avoid the inevitable
25   space charge effects which result in a small drift in phase. It is also unrealistic to expect that the parameters of the trap can, in manufacture, be kept to such a tight tolerance that there is no perturbation to the ideal field (1) at all. Thus, the most preferred realistic scenario is that the
30   parameters of the trap are optimised so that the electrostatic field is approximately hyper-logarithmic and has a perturbation to it W which is dependent on r and/or $\phi$

only.  In this case, other than the small time dependent
phase shift resulting from space charge, the phase shift of
ions over time should be zero.

In the case where the perturbation W depends upon z as
5    well as, or instead of, r and/or $\phi$, it is desirable to
ensure that the trap parameters are optimised so that there
is phase spreading, rather than phase bunching, over time,
and that the phase spreading is at a sufficiently low rate
that the time taken for the net phase spread to exceed $\pi$
10   radians is  greater than an acceptable measurement time
period $T_m$.  This is not to imply that there can be no phase
bunching at all, and indeed a small degree of phase bunching
even without any phase separation may produce an acceptable
performance, only that it is preferable that  at least a
15   majority of non-bunched ions  survive with a phase spread
less than $2\pi$ radians for the entire measurement period.
The difficulties that result from phase bunching become less
and less pronounced as the growth of $\Delta\theta$ over the
measurement time scale $T_m$ decreases.

20       There are, of course, a large number of parameters that
vary in the construction of an electrostatic trap, however,
a number of particularly desirable optimisations have been
identified.  These have been implemented and are described
now with reference to Figures 4 to 7.  Referring first to
25   Figure 4, a schematic side view of an Orbitrap 80 is shown.
The operation of the Orbitrap is as previously described and
as set out in detail in, for example, US-A-5,886,346.  The
Orbitrap 80 comprises an inner electrode 90 (shown in end
section in Figure 1) and split outer electrodes 400, 410.
30   As may be seen in Figure 4, the electrodes are shaped, so
far as is possible within manufacturing tolerances, to have
the hyper-logarithmic shape of Equation (1).  Within the

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outer electrode 410 is a deflector 420.  Ions are introduced
into the trapping volume defined between the inner electrode
90 and outer electrodes 400, 410 through a slot 425 between
the outer electrodes 400, 410.

5        End cap electrodes 440, 450 contain ions within the
trapping volume.  An image current is obtained using a
differential amplifier 430 connected between the two outer
electrodes 400, 410.

         In one embodiment, the outer electrodes 400, 410 are
10   stretched in the axial (z) direction.  Axial stretching of
the outer electrodes relative to the ideal shape improves
mass accuracy over a wide mass range for ions injected using
electrodynamic squeezing as described by Makarov in
Analytical Chemistry Vol. 72 (2000) pages 1156-1162.
15   Moreover, the inner electrode 90 may be radially compressed
around its axis of symmetry in order to introduce a
perturbation that results in gradual phase
spreading.Additionally or alternatively, voltages may be
applied to the end electrodes 440, 450.

20       Since the ions exhibit harmonic motion along the z-axis
of the trap, the ions exhibit turning points  towards the
extremities of the trap (+/-z).  At these points, the ions
are moving relatively slowly and thus experience the
potential towards the trap extremities (in the axial
25   direction) for longer than they experience the potential in
the vicinity of the centre slot 425 (Fig. 5).  The ions at
these turning points are also relatively close to the outer
electrodes. The result of this is that the shape of the trap
in the vicinity of the turning points has a relatively
30   significant impact on the ions. On the other hand, these
turning points are axially inward of the outer extremities
of the trap. In consequence, the shape of the trap at its
axial extremities (outside of the turning points) has

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relatively limited effect upon the ions, since it is only
the far field of these regions that affect the ions in the
region of the turning points. In particular, the shape of
the trap over the last 10% of its length is largely
5    irrelevant.

As may be seen in Figure 5, the ion injection slot 425
is axially central. The ions pass this point at maximum
velocity and thus spend statistically less time there. They
are also well spaced from the outer electrodes at that
10   point. Thus, whilst the shape of the trap there has some
impact on the ion trajectories, it is not so critical as the
shape of the trap at the turning points. On the other hand
the ion injection slot 420 in the embodiment of Figure 4 is
located away from the central (z) axis, and is generally in
15   the region of one of the ion turning points. Thus the shape
of the trap in the region of the slot 420 is relatively
critical to trap performance.

As a related issue, it transpires that there is no
apparent need to provide compensation (at the electrode
20   extremities) for the truncation of the electrodes relative
to their ideal infinite extent.

Figure 5 shows an alternative arrangement to the
embodiment of Figure 4, although it is to be understood that
the modifications and features of Figure 5 are by no means
25   mutually exclusive with those applied to the arrangement of
Figure 4. Nevertheless, features common to Figures 4 and 5
have been labelled with like reference numerals.

In Figure 5, a spacer electrode 460 is mounted between
the outer electrodes 410, 420 and a voltage may be applied
30   to this. In general terms, employing a spacer between the
outer electrodes so as to shift them apart may be desirable.

Figure 6 shows still another embodiment. Here, the
outer electrodes 400, 410 are segmented into multiple

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sections 400', 400", 410', 410". In that case, bias
voltages may be applied to the segments. Each of the
segment pairs may also be used for ion detection in this
mode, allowing detection at multiples of ion frequency. For

5    example, a  triple frequency can be detected in the
arrangement of Figure 6 without the loss of signal to noise
ratio, if the differential signal is collected between
connected segment pairs 400'-410', and 400"-410". As
another example, the signal may be detected between 400' and

10   410" (for example, with segment 400" and segment 410'
grounded or biased), providing strong third harmonics of
axial frequency, albeit at a lower signal to noise ratio. An
increase in the detection frequency provides a benefit of
higher resolving power within the limited detection time $T_m$.

15   This is particularly useful for higher mass to charge ratio
ions.

Turning finally to Figure 7, still a further embodiment
of an electrostatic trap 80 is shown. As with the
arrangement of Figure 4, the Orbitrap 80 comprises a pair of

20   outer electrodes 400, 410 with a differential amplifier 430
connected across these. The outer electrode 410 also
includes a compensation electrode 420.

The inner electrode 90, however, is split into two
segments 90', 90". Bias voltages may be applied to the

25   segments. In addition to the segmentation, a spacer
electrode 470 may also be included, preferably on the axis
of symmetry (z=0). Different segments could, of course,
also be employed for detection with or without the outer
electrodes.

30   Although a number of different embodiments have been
shown, it is to be understood that these are simply examples
of adaptations to the dimensions, shape, size, control and
so forth of the trap, to minimise the effect of

perturbations that cause phase bunching and to maintain
perturbations which optimise (i.e. minimise) the rate of
increase of phase separation over the measurement period $T_m$.
Any of the combinations described in connection with Figures

5     4 to 7 may be combined.  Other means may be employed to
produce multipole fields, that is, fields containing terms
proportional to $z^n$, where n>2.  Moreover, the Orbitrap 80
may be immersed in a magnetic field which provides mass
dependent correction of aberrations.  This may be especially

10    effective for low mass to charge ratio ions that usually
suffer the greatest scattering during extraction from an
external storage device, an effect which is described in
further detail in WO-A-02/078046.

It is also to be appreciated that the voltage on the

15    deflection electrode 420 (Figures 4 and 7) should be chosen
in such a way that the deflection electrode itself
contributes a minimal non-linearity to the field. In general
terms, the geometric distortions described in connection
with Figures 4 to 7 have a magnitude of a few, to a few tens

20    of, microns.

Empirically, some optimal ranges for geometric
distortions have been determined and are listed below.  Once
more, it is stressed that these are experimentally observed
observations that result in a limitation in the phase spread

25    and are in no way intended to be limiting of the general
inventive concept.  In the following list, the dimension D2
is (as indicated in Figure 6) the inner diameter of the
outer electrodes 400, 410, at the axis of symmetry (z=0).
The dimension D1 is the outer diameter of the central

30    electrode 90, again the axis of symmetry (z=0).

(A)   For present day machining technology, the optimal
inner diameter of the outer electrodes D2 is between 20 and
50 mm, optionally 30 mm ± 5 mm;

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(B)    In preference, D1<0.8D2, optionally 0.4D2 ±
0.1D2;   (so that the inner electrode diameter D1 is
preferably 12 mm when D2 is as in (A) above).

(C)    The parameter $R_m$ in Equation (1) and Equation (4)
5    is preferably in the range 0.5D2<$R_m$<2D2, and optionally
0.75D2 ± 0.2D2;

(D)    The width of the entrance slot 425 (Figure 4, for
example), in the z direction, should in preference lie in
the range 0.01D2 to 0.07D2 and optionally between 0.02D2 and
10    0.03D2, and, in the direction perpendicular to z (that is,
in a direction looking into the page when viewing Figure 4,
for example), should be less than 0.2D2, optionally between
0.12D2 and 0.16D2;

(E)    The overall inner length of the system should be
15    greater than twice (D2-D1), and most preferably greater than
1.4 times D2;

(F)    The accuracy of the shape of the outer electrodes,
relative to the hyper-logarithmic form of Equation (1)
should be better than $5 \times 10^{-4}$D2, and optionally better than
20    $5 \times 10^{-5}$D2; where the inner diameter of the outer electrode is
30 mm, the total deviation is preferably 7μm or better.  It
has been found that the trap performance is better when the
diameter of the outer electrodes is either nominally ideal
or is slightly oversized (i.e. not undersized).  By contrast
25    the performance is enhanced when the central electrode is
undersized (that is, too thin) by a few micrometers when the
central electrode is of nominal maximum diameter 6 mm, a
slightly (-4μm to -8μm) thinner electrode improves trap
performance.  Central electrodes of the correct nominal
30    diameter or larger appear to result in a trap of reduced
performance.  One feasible explanation for this is that a
slightly undersized central electrode introduces a negative
high powered term (such as a fourth or higher power term) in

the potential distribution parallel to the z-axis at a given diameter.  The resultant slightly "flattened" potential, provided not too large, exerts a sufficient but not excessive force on the ions to prevent the unwanted "self-

5   organization" of ions described above.  In other words, the $-x^4$ or other high order term introduced by a slightly undersized central electrode appears to promote a slow phase spread.  This is a desirable situation - the phase does spread (which prevents bunching) but not too fast to prevent

10  ion detection in an acceptable time scale.

(G)   The gap between the outer electrodes should be less than 0.005D2, in preference, and optionally around 0.001D2.  It has however been ascertained that the axial gap between the outer electrodes may be 2-4µm too large without

15  destroying the trap performance;

(H)   The shift of the central electrode along z-axis in either direction should be less than 0.005D2, and optionally less than 0.0005D2;  in the 'r' direction the central electrode shift should be less than 0.01D2 and most

20  preferably <0.001D2;

(I)   The additional axial stretching of the outer electrodes relative to the ideal shape should be preferably in the range of 0 to $10^{-3}$D2, and optionally less than 0.0003D2;

25  (J)   The degree of allowed tilt of the central electrode should be less than 1% of D2 and preferably less than 0.1%D2;

(K)   The allowed misalignment of the outer electrodes should be less than 0.003D2 and preferably less than

30  0.0003D2;

(L)   The allowed systematic mismatch between outer electrodes should be less than 0.001D2 and preferably less than $5 \times 10^{-5}$D2.  In general, the mirror symmetry between the

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injection and detection sides of the Orbitrap appears to be
very important. Typically, it is desirable that the maximum
diameters of the left and right outer electrodes match each
other to within around 0.005% which corresponds to 1-2μm in
5    a 30 mm diameter trap; and

(M)    The allowed surface finish should be better than
$2\times10^{-4}D2$ and optionally less than $3\times10^{-5}$ times D2. However,
small, random variations in surface smoothness seem to have
a beneficial effect. In other words, random surface defects
10   appear to provide improved performance whereas long range
(systematic) variations reduce performance.

It will be apparent from the foregoing (and with
reference to the examples described below in connection with
Figures 8, 9 and 10) that the different parameters, do not
15   generally result in a 'perfect' or 'useless' trap but
instead combine with one another in a complicated manner to
present a trap that lies  in a range between these two
extremes. Observations nevertheless confirm that, where the
parameters are within the ranges specified below, acceptable
20   traps are produced; where the parameters are optimised to
the magnitudes listed, currently good traps with correct
peak shapes and positions are produced. Moreover, of the
above, items (D), (E), (F), (G) and (H) appear to contribute
most markedly to a degrading perturbation which forces
25   dominance of phase bunching. Thus particular care should be
taken in construction, to minimise the amplitudes or
dimensions within the preferred ranges.

The foregoing description has explained a feasible
physical basis for a degradation in the performance of a
30   real electrostatic trap, in terms of perturbations to the
ideal electrostatic field and the requirement that there
should be at least a proportion of the ions which are not
phase-bunched but which do not phase-separate too rapidly,

if acceptable trap performance is to be realised.  By
controlling the parameters of the trap, for example by
closely controlling the ranges of the parameters set out in
(A) to (M) above, the degree to which any real trap meets
the criterion of the present invention (minimising the rate
of increase of phase spread) can be determined directly.
However, again empirically, a number of indicators of likely
trap performance (that is, likelihood that the specific
requirement regarding rate of increase of phase spreading
over the measurement period $T_m$) exist.

Various elements have several isotopes which exist in
nature at a well known and defined ratio of relative
abundances.  For example, carbon has two stable isotopes,
$^{12}C$, $^{13}C$ which exist in nature in the ratio of approximately
98.93% and 1.07% respectively.  By obtaining a mass spectrum
of the carbon isotopes using a candidate electrostatic trap,
the measured relative abundances of the isotopes can provide
an indication of the likely suitability of that candidate
trap that is, the likelihood that it will meet minimum
performance requirement. The consequence of a badly-
performing trap, in which non-self-bunching signals decay
very quickly (over time $t<<T_m$) results in only self-bunched
signals (such as in curve 340 of Figure 3) surviving.
Although such self-bunched signals give the impression of
acceptability, since peaks in a mass spectrum are narrow and
peak intensity is good, the smaller isotopic peak for $^{13}C$
appears much smaller than natural abundance ratios would
predict. It may also be split into two or more sub peaks.

As a rule of thumb, therefore, if a real trap indicates
an apparent natural abundance of $^{13}C$ of less than about 0.7%
(where its predicted abundance should be in the region of
1.07%), the trap would typically be rejected.

Figures 8a-d and 9a-d show plots of ion abundance
against m/z (i.e., mass spectra) for m/z around 195 and m/z
around 524, respectively, with differing amounts of field
perturbation.  In particular, Figure 8a shows a zoom-in of
5    mass spectrum at nominal mass 195. Figure 9a shows a mass
spectrum with a main peak at nominal mass 524 and two
smaller peaks at nominal masses 525 and 526 indicative of
the presence of two isotopes.  The label for each peak lists
m/z to 4 decimal places together with the resolving power of
10.  the Orbitrap. The relative abundances of these two isotopic
peaks (normalized to the intensity of the main peak) are 26%
and 4% respectively, in the ideal limit.

Figures 8a and 9a are obtained from an Orbitrap that
operates with excellent parameters, that is, the rate of
15   decay of the transient (or, put another way, the rate of
increase in phase separation) is very slow.  Here, peak
resolution is limited by the length of the stored transient
(i.e. the measurement time $T_m$), which in Figures 8a and 9a
is 0.76 seconds.

20        Figures 8b and 9b show mass spectra over the same
ranges, using the same ions, but with a slight non-linearity
in the electrostatic trapping field resulting in a
discernable but acceptable amount of phase spreading over
the measurement time $T_m$.  It will be noted in Figure 8b that
25   the main peak has developed small wings on each side and
that the measured peak position is also shifted very
slightly to a lower apparent m/z.  Figure 9b also shows a
very slight shift in the peak positions of the main peak and
the two isotopes, and also the relative abundances of the
30   isotopes are slightly different from those predicted.
Nevertheless, the peaks do show good shape and there is no
peak splitting.

Turning to Figures 8c and 9c, the mass spectra of an
Orbitrap with an unacceptably rapid phase expansion are
shown, again for the same ions as were employed in respect
of Figures 8a, 8b, 9a and 9b respectively. In Figure 8a,

5     the main peak is seen to be badly suppressed (abundance less
than 40% of the 'true' abundance illustrated in Figure 8a)
and with a larger number of adjacent peaks which alter the
true shape of the peak as well. Figure 9c illustrates the
problems of rapid phase expansion (leaving just phase

10    bunched ions to be detected within a short amount of time,
relative to the total measurement time $T_m$) as well. The
main peak is suppressed (although in Figure 9c its intensity
has been renormalized to 100%) and the two isotopes show a
much higher relative abundance than they should (around 37%

15    and 7% respectively, compared with theoretical values of 26%
and 4.5%). Inset into Figure 9c is a zoomed part of the
spectrum around the main peak, contrary to the correct
appearance (that is, the peak shape of Figures 9a and 9b).

        Finally, for completeness, Figures 8d and 9d show mass

20    spectra where a very large non-linearity exists or is added
to the trap so that any ions that are not phase bunched
become undetectable within a very short timescale ($<<T_m$).
In Figure 8a the poor peak shape is apparent - the narrow
'spike' is a result of the phase bunched ions and the

25    smeared signal either side of that spike is a result of the
rapidly decaying phase spreading signal. The mass spectrum
of Figure 9d demonstrates similar problems with the main
peak (a sharp spike resulting from phase bunched ions
together with a wide spread of minor peaks surrounding the

30    main peak). Moreover, the smaller isotopic peaks are also
severely split (into a 'spike' and a spread of side bands)
due to the phase bunched and rapidly phase spreading ions

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respectively.  The relative magnitudes of the main and
isotope peaks are also nowhere near the theoretical values.

Figures 10a and 10b show transients (in the time
domain) from traps with rapidly and slowly increasing phase
5    spreads, respectively. It will be seen in Figure 10a how the
transient clearly contains a rapidly decaying component
(over approximately 200 msec) and a slower decaying
component (beyond 200 msec or so).  This is what results in
the split peaks of Figures 9c and 9d, for example.  Figure
10   10b, by contrast, shows a transient with a much more gradual
decay, even over 3 seconds (note the difference in scales on
the 'x' axis, between Figures 10 and 10b).  The transient of
Figure 10b, once transformed into a mass spectrum, shows
good mass accuracy, peak shape and so forth, as illustrated
15   in Figures 8a, 8b, 9a and 9b.

Another indicator of poor trap parameters is the
presence of an unusual non-linearity in the mass
calibration.  For example, if a non-monotonous dependence is
noted in the mass range, rather than a linear function, it
20   is generally concluded that the trap parameters will not
meet the requirement for the maximum rate of phase
spreading.  Good Orbitraps tend to have a specific
dependence of mass deviation on ion injection energy:  from
0 to 40 ppm per 150V injection energy increase appears to be
25   indicative of a functional trap.  Those traps exhibiting a
negative slope (of about -5 to -10 ppm or more) do not
generally work.  To an extent this can be mitigated
(compensated) by the use of a larger spacer electrode 460
(Figure 5), which results in the outer electrodes 410, 420
30   being moved outwards, which in turn weakens the field at the
trap edges.

Finally, as explained above, the presence of split
peaks, resulting from the complex structure of the

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perturbation W, normally provides a good clue that the
performance of the trap in general will not be acceptable.

To optimise the stability of the construction of an
electrostatic trap, having optimised the parameters

5    themselves such as in accordance with (A) to (M) above, it
is preferable to use temperature invariant materials in the
design, such as Invar$^{(TM)}$ for the trap itself, and quartz or
glass for insulation. In addition, high or ultra-high
vacuum should be maintained within the volume traversed by

10   the ions.

It is of course to be understood that the invention is
not limited to the various embodiments of Orbitrap described
above, and that various modifications may be contemplated.
For example, as described in our copending application no

15   GB0513047.1, the contents of which are incorporated by
reference in their entirety, the Orbitrap electrodes may be
formed from a series of rings rather than one or more solid
electrodes. In that case, in order to introduce the
desirable perturbation W to the ideal hyperlogarithmic

20   electrostatic potential $U(r,\varphi,z)$, the rings can be
manufactured to have a shape that conforms to an
equipotential of the perturbed field $U'(r,\varphi,z)$. On the other
hand, it may be preferable as well or instead to separate or
compress some or all of the rings relative to one another in

25   the axial (z) direction to create the same effects as are
listed in (A)-(M) above. For example, spreading the outer
electrode rings relative to the ideal equipotential mimics
the desirable "flattened" shape discussed in (F) above.
Compressing the inner rings together likewise mimics the

30   smaller diameter inner electrode arrangement that is
beneficial.

Indeed, the invention is not limited just to the
Orbitrap. The ideas may equally be applied to other forms of

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EST including a multi-reflection system with either an open
geometry (wherein the ion trajectories are not overlapping
on themselves after multiple reflections) or a closed
geometry (wherein the ion trajectories repetitively pass

5    through substantially the same point). Mass analysis may be
based on frequency determination by image current detection
or on time-of-flight separation (e.g. using secondary
electron multipliers for detection). In the latter case, it
will of course be apparent that a phase spread of $2\pi$ radians

10   corresponds with a spread of time-of-flights of ions of one
period of reflection. Various examples of ESTs to which the
invention may be applied are described in the following non
limiting list: US-A-6013913, US-A-6888130, US-A-2005-
0151076, US-A-2005-0077462, WO-A-05/001878, US-A-

15   2005/0103992, US-A-6300625, WO-A-02/103747 or GB-A-
2,080,021.